Supporting Information

Ultrasensitive luminescent nanothermometer in first biological window based on phonon-assisted thermal enhancing and thermal quenching

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Experimental section

Chemicals. $Ln(NO_3)_3$ stock solutions were prepared by dissolving Yb_2O_3 (99.99%, Aladdin), Tm_2O_3 (99.99%, Aladdin) and Er_2O_3 (99.99%, Aladdin) into hot nitric acid in stoichiometric proportions. Na_2MoO_4 (99%), $YbCl_3 \cdot 6H_2O$ (99.99%), $TmCl_3 \cdot 6H_2O$ (99.99%) and $(NH_4)_2HPO_4$ (99%) were purchased from Beijing HWRK Chem Co., LTD.

Sample Preparation. $NaYb(MoO_4)_2$: xTm^{3+} nanosheets were synthesized by hydrothermal method with further calcination. The stoichiometric amounts of $Ln(NO_3)_3$ stock solutions were dissolved in the appropriate amount of deionized water. Next, the stoichiometric amounts of Na_2MoO_4 with $Ln(NO_3)_3/Na_2MoO_4=1/3$ were dissolved in the appropriate amount of deionized water and dropped into the above solution. The pH of the mixed solution was adjusted to 5 with diluent nitric acid and sodium hydroxide to form a white colloidal solution and stirred for 1 h. Then the mixture was transferred into a Teflon-lined stainless steel autoclave, and maintained at 180 °C for 24 h. The precipitates were obtained by centrifugation and washed with deionized water and ethanol. After drying at 60 °C for 10 h, the nanosheets were obtained by calcining the precipitates at 600 °C for 6 h. The synthesis of $NaYb(MoO_4)_2$: $5\%Er^{3+}$ sample was similar except that $Er(NO_3)_3$ stock solution was required.

$YbPO_4$: $1\%Tm^{3+}$ nanoparticles were synthesized by the coprecipitation method with further calcination. The lanthanide chlorides ($YbCl_3 \cdot 6H_2O$ and $TmCl_3 \cdot 6H_2O$) were stoichiometrically dissolved in appropriate amount of deionized water. Then the stoichiometric amounts of $(NH_4)_2HPO_4$ dissolved in appropriate amount of deionized water were dropped into the above solution and stirred for 7 h. The precursors were obtained by centrifugation and washed with deionized water and ethanol, and then dried at 70 °C for 10 h. Finally, the dried precursors were calcined in air at 1200 °C for 2 h to yield the final nanoparticles.

Cytotoxicity assay. A standard MTT assay was utilized to assess the cytotoxicity of $NaYb(MoO_4)_2$: 1%Tm^{3+} sample in Hela cells. The cells were incubated for 24 h with 5% CO_2 at 37 °C to attach them to the wells. Then the sample was introduced into the wells and incubated for another 24 h with a set series of concentrations.

Characterization Techniques. The crystallographic phases of all samples were determine by XRD patterns on a Bruker D8 Focus diffractometer equipped with Cu Kα radiation (λ = 0.15405 nm). The morphologies were studied via a field emission scanning electron microscope (SEM, Philips XL30) and a transmission electron microscope (TEM, JEM-2200FS). The Fourier transform infrared spectra were collected by a Bruker TENSOR 27 FT-IR spectrometer. The luminescence spectra were collected by an Andor SR-500i spectrometer (Andor Technology Co, Belfast, U.K.) equipped with a SR830 DSP lock-in amplifier and a CCD detector under the excitation of a 980 nm diode laser. The temperature evolution emission spectra of samples were obtained with the assistance of a copper-constant thermocouple and temperature control system (TAP-02, orient-KOJI). The absorption spectra were measured with a Shimadzu UV-3101PC scanning spectrophotometer. The quantum yield was measured on a fluorescence spectrometer (FLS1000, Edinburgh) equipped with an integrating sphere under the excitation of 980 nm (5 W/cm^2).

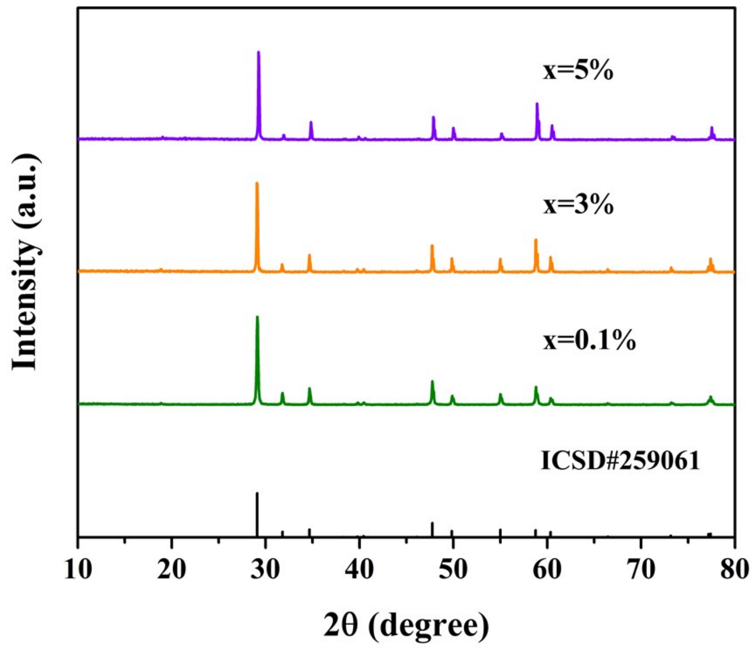

Figure S1. The XRD patterns of $NaYb(MoO_4)_2$: xTm^{3+} samples.

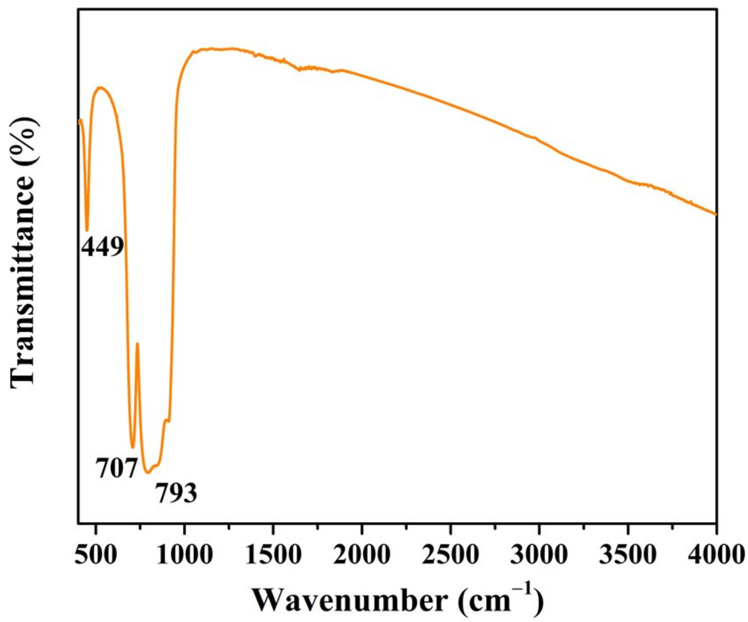

Figure S2. The Fourier transform infrared spectrum of $NaYb(MoO_4)_2$: $1\%Tm^{3+}$ nanosheets.

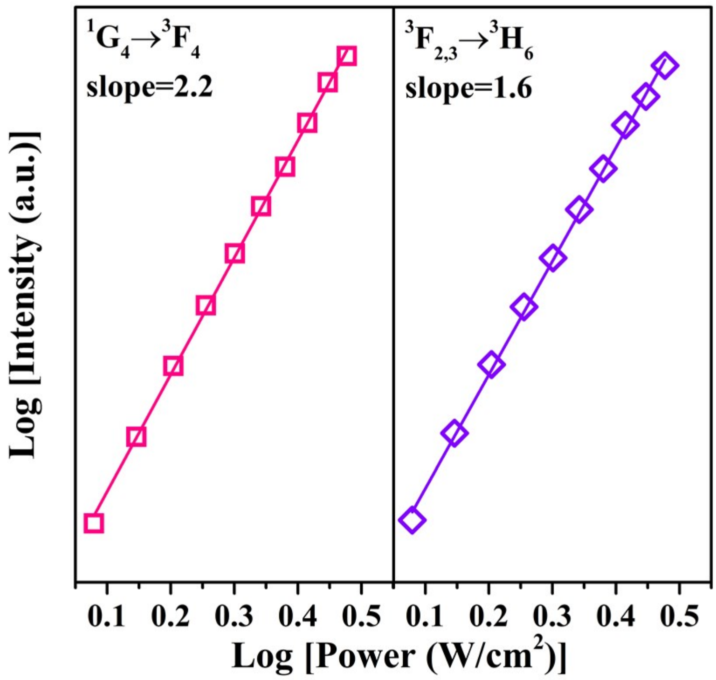

Figure S3. Double-log intensity-power slopes of $^1G_4 \rightarrow ^3F_4$ and $^3F_{2,3} \rightarrow ^3H_6$ transitions for $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets.

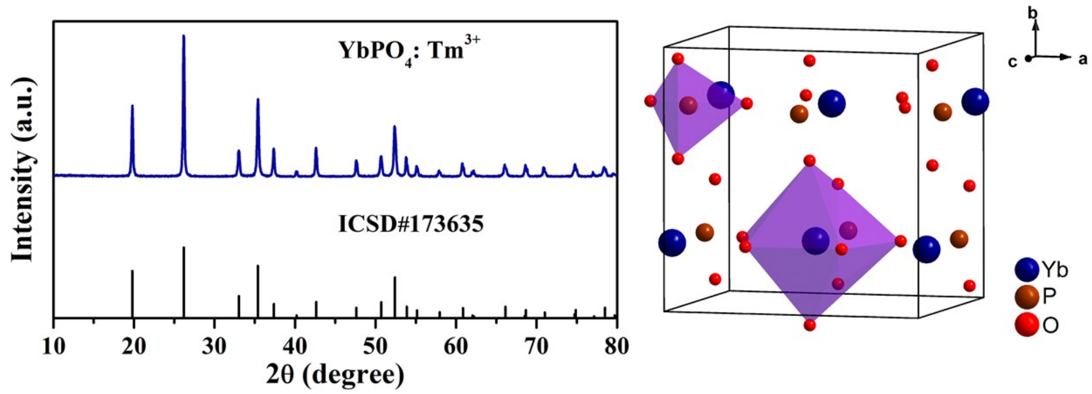

Figure S4. The XRD pattern of $YbPO_4$: 1%Tm^{3+} sample, and the schematic crystal structure of tetragonal phase $YbPO_4$.

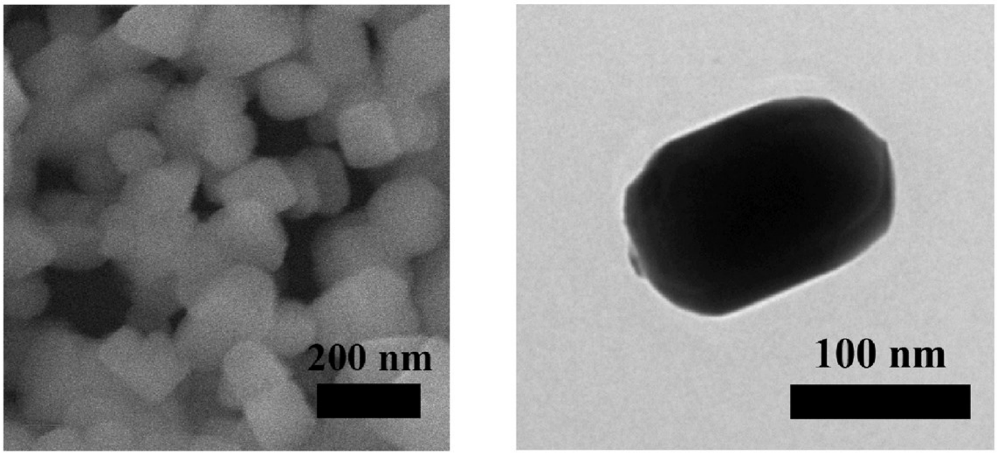

Figure S5. The SEM and TEM images of $YbPO_4$: 1%Tm^{3+} nanoparticles.

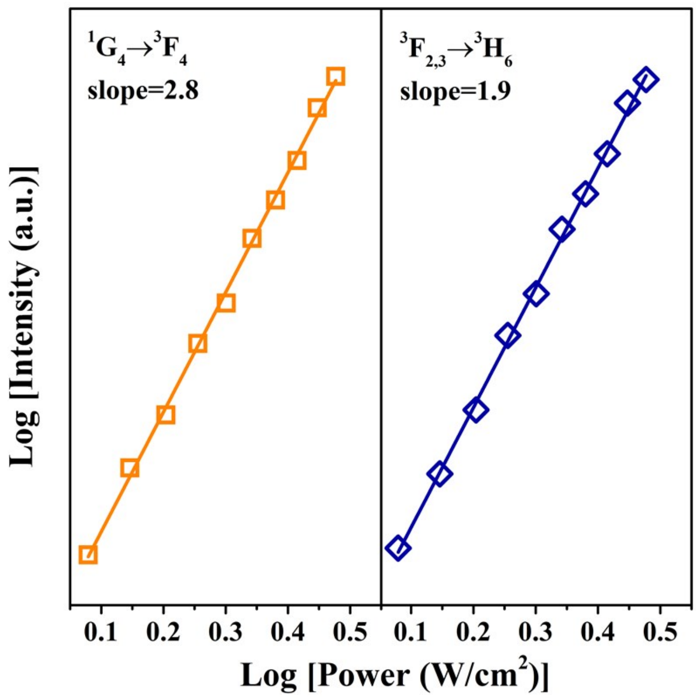

Figure S6. Double-log intensity-power slopes of $^1G_4 \rightarrow ^3F_4$ and $^3F_{2,3} \rightarrow ^3H_6$ transitions for $YbPO_4$: 1%Tm^{3+} nanoparticles.

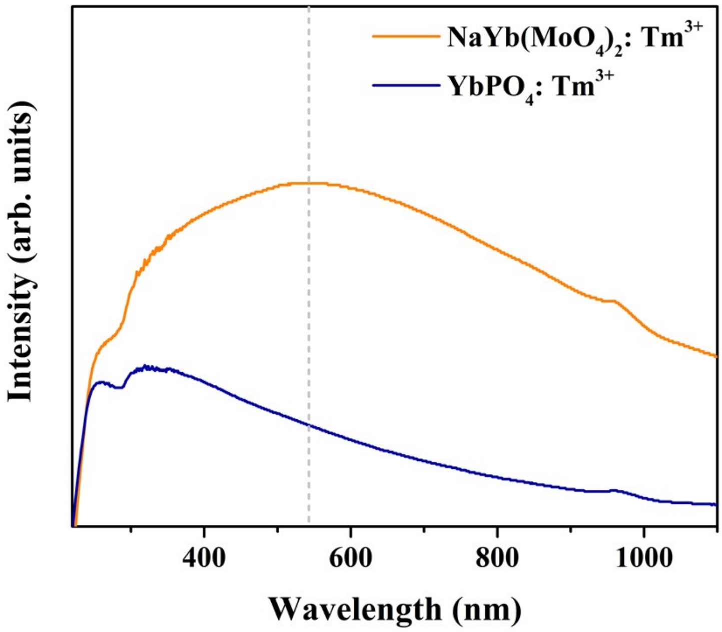

Figure S7. The absorption spectra of aqueous suspensions of $NaYb(MoO_4)_2$: 1%Tm^{3+} and $YbPO_4$: 1%Tm^{3+} samples.

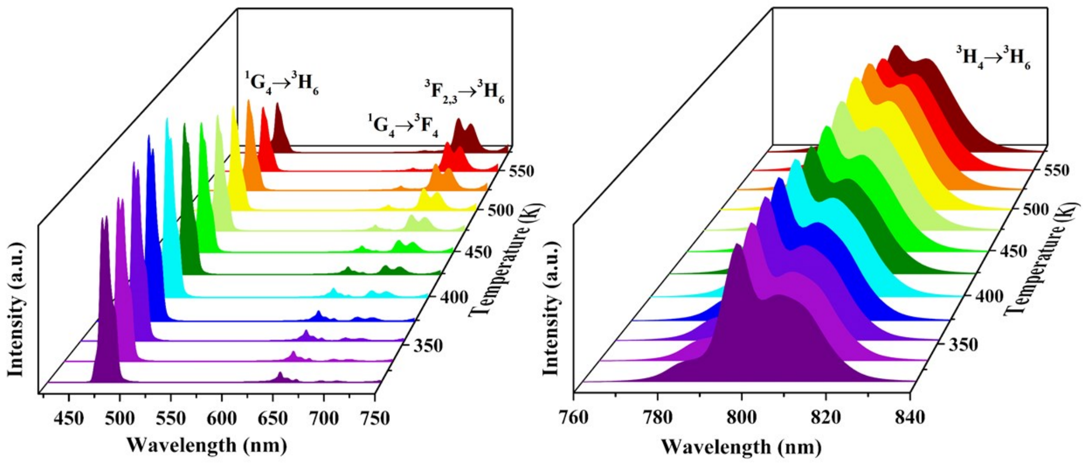

Figure S8. The temperature evolution emission spectra in the 313–573 K range of $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets.

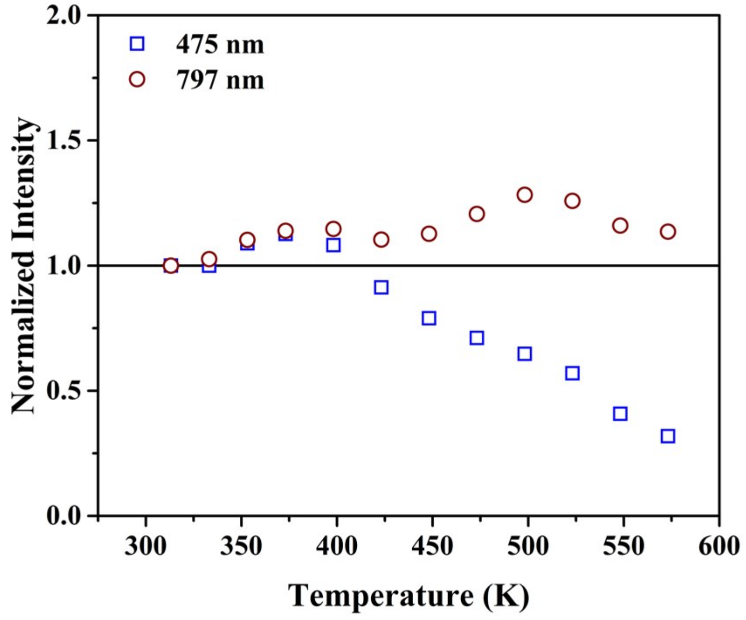

Figure S9. The normalized integrated intensities with temperature of corresponding transitions for $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets.

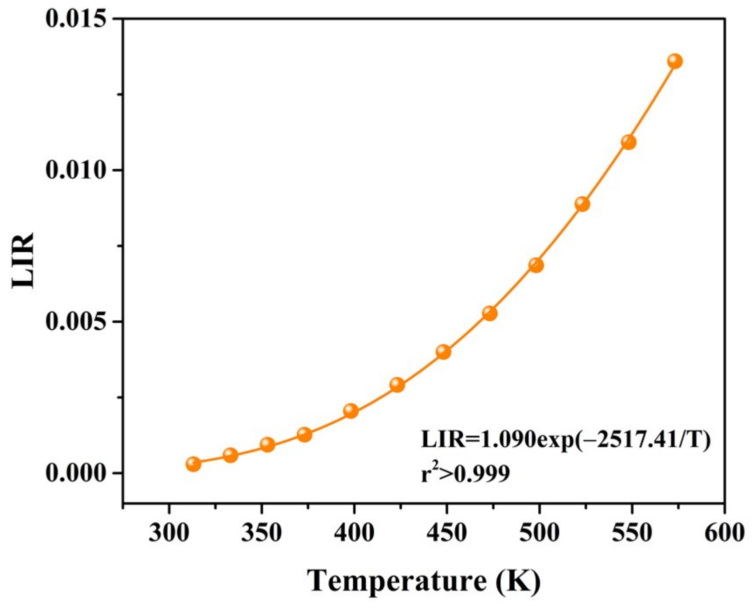

Figure S10. The thermally coupled thermometry based on $^3F_{2,3}$ and $^3H_4$ levels of $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets.

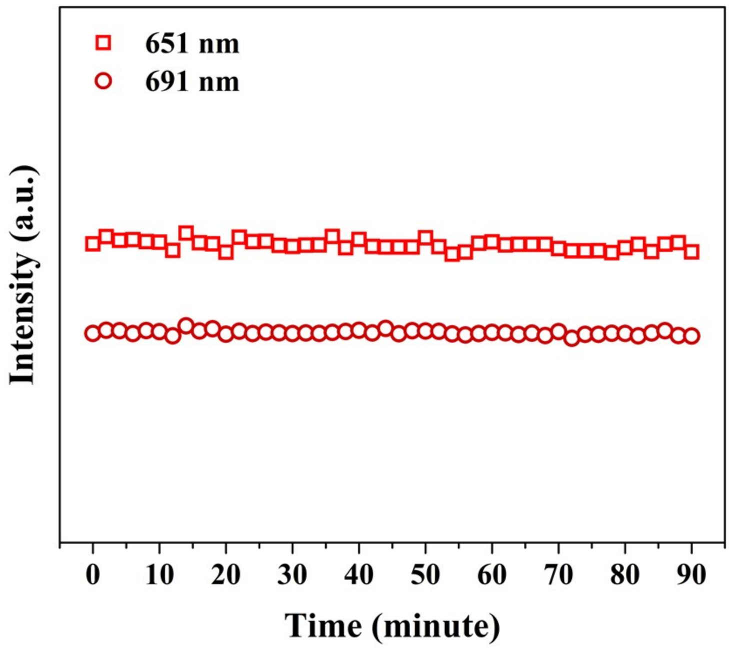

Figure S11. The time-dependent integrated intensities of $^1G_4 \rightarrow ^3F_4$ and $^3F_{2,3} \rightarrow ^3H_6$ emissions of $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets at 373 K.

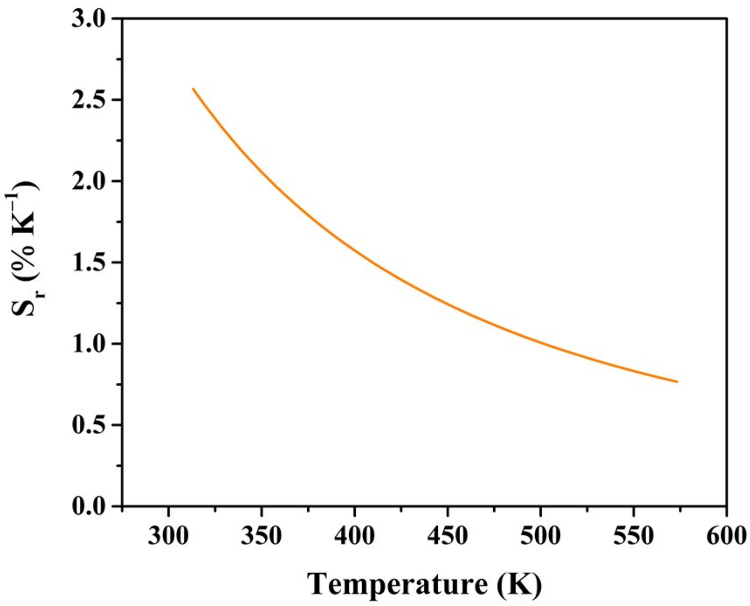

Figure S12. The S_r of thermally coupled thermometry based on $^3F_{2,3}$ and $^3H_4$ levels of $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets.

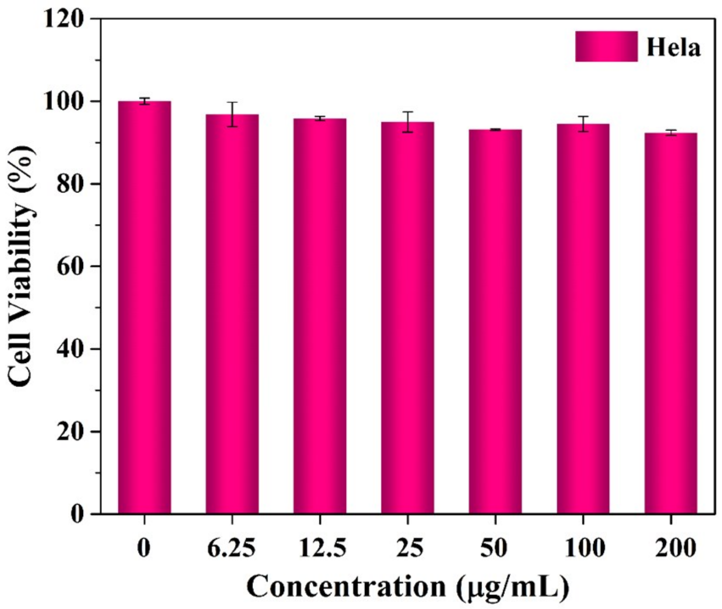

Figure S13. The cell viabilities of Hela cells incubated with different concentrations of $NaYb(MoO_4)_2$: 1%Tm^{3+} sample for 24 h.

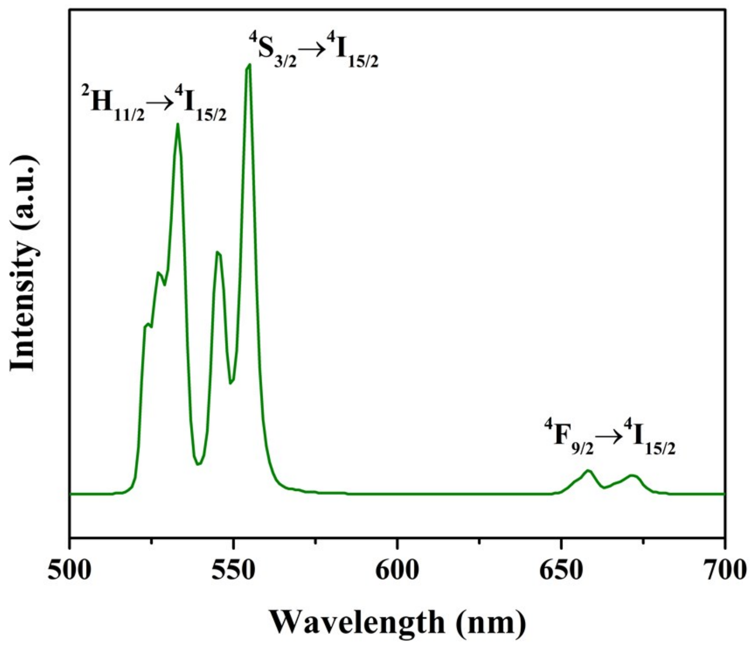

Figure S14. The emission spectrum of $NaYb(MoO_4)_2$: 5%Er^{3+} nanosheets under the 980 nm excitation.

Table S1. The fitting parameters of calibration curve for $NaYb(MoO_4)_2$: 1%Tm^{3+} nanosheets.

Parameter	Value	r^2
a	−0.4078±0.0380	
b	0.0061±0.0003	0.99994
c	70.48±0.47	

Table S2. The fitting parameters of power-dependent *LIR* values at different temperature of $NaYb(MoO_4)_2$: 1%Tm^{3+} nanothermometers.

Temperature (K)	e	Δn	r^2
333	0.6413±0.0035	−0.6570±0.0083	0.9987
373	1.3367±0.0060	−0.6340±0.0068	0.9991
423	3.3129±0.0278	−0.5190±0.0123	0.9954